Fullerene based materials for ultra-low-*k* application

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***Abstract* – Fullerene-based materials are considered to be a candidate for ultra-low-*k* material applications. We have incorporated fullerene C_{60} into a siloxane material by means of the sol-gel method. Thickness of obtained film was investigated by atomic force microscope, dielectric constant was measured by the capacitance-voltage characterization (CV). Interactions between the components within the films were investigated by using X-ray photoelectron spectroscopy and near edge X-ray absorption fine structure spectroscopy. We found that the ratio of carbon, oxygen and silicon atoms within obtained film equals 2.7:1.9:1. The microscopic and CV investigations show that the sample's composition is inhomogenous although the fullerene's concentration within the material is low. However, dielectric constant is in the range of 2.3 to 2.5.**

INTRODUCTION

The rapid development of microelectronic performance follows the Moore's law predicting that the number of transistors in the integrated circuits increases twice every eighteen months [1]. However, because of the huge transistor's density in the advanced integrated circuits its size has to be reduced what makes the circuits faster while at the same time the overall resistance-capacitance (RC) delay increases. One of the strategies of increasing the speed of microelectronics' devices is to reduce the RC delay. [2, 3]. One of the strategies to reduce RC delay is introduction of low-*k* materials as an isolation between the nano-wires in microelectronic devices. From a theoretical point of view, fullerene materials are very promising candidates for low-*k* dielectric materials. The results of calculations show that cross-linking of C_{60} fullerenes by suitable bridge molecules is an efficient way to construct materials with ultra low dielectric constant [4]. Fullerenes, since theirs' discovery in 1985, demonstrated a various applications on many fields of science, however there are few reasons such as: ability to form clusters, low solubility and thermal stability, that imposes theirs' modification with other materials in order to enable the practical application [5, 6]. In this paper we report results of spectroscopic investigations of sample obtained by incorporation of C_{60} molecules into the material produced by the means of the sol-gel method.

EXPERIMENTAL

A. Materials

Phenyl triethoxysilane (PhTriEOS) from Aldrich (98% purity), methyl trimethoxysilane (MeTriMOS) from Fluka (purum) were used. Ethanol (EtOH), acetone and toluene were obtained from POCh (Poland) and used as received. Hydrochloric acid (HCl), available from POCh was diluted in distilled water before use. C_{60} fullerenes (99+% purity) were obtained from MER Corporation (Arizona, USA) and used as received as well.

B. Sample preparation

A basic sol solution was prepared by mixing PhTriEOS : MeTriMOS : EtOH : HCl in molar ratio 1.00 : 1.22 : 7.77 : 1.03×10^{-3} respectively. Then a saturated solution of C_{60} in toluene was prepared with concentration 2.80 mg/ml. C_{60} solution was mixed with the basic solution PhTriEOS : C_{60} in molar ratio 1.00 : 3.50×10^{-3}, respectively. Afterwards the substrate was coated from such a solution and dried. The detailed procedure, previously used for preparation of similar thin film obtained from different precursors, is described in literature [7]. As a substrate a monocrystal silicon wafer with a 100 nm layer of SiO_2 was used. The substrate was rinsed in acetone, distilled water and finally in ethanol, then dried at room temperature before coating.

C. Measurements

X-ray photoelectron spectroscopy (XPS) measurements were done using SPECS GmbH X-Ray source (Mg Kα 1253.6 eV) and energy analyzer made by Leybold-Heraeus.

Near edge X-ray absorption fine structure spectroscopy (NEXAFS) technique needs a tuneable X-ray source, and therefore, this technique is exclusively used at synchrotron radiation source. We have done our measurements at the at the undulator beamline U49/2-PGM2 at Bessy II, Berlin-Adlershof. The total electron yield (TEY) signal was measured by using sample current. At the same time, the total fluorescence yield (TFY) was measured with a fluorescence detector. The NEXAFS spectra were normalized to the X-ray intensity I_0, measured on a diode or Au mesh. The TFY-signal shows higher bulk sensitivity than TEY, because the X-ray photons are significantly less attenuated when penetrating through the film. This technique is often used to analyse the

chemical bonding, as shape of the absorption profile differs characteristically for different unoccupied states.

Fourier transform infrared spectroscopy (FTIR) measurements were performed by Thermo scientific FTIR 6700. The absorbance spectra were collected in the range of 400-4400 cm^{-1}. Each measurement was an average of 64 scans with a resolution of 4 cm^{-1}.

Thickness measurements were conducted by Veeco CPII atomic force microscope (AFM) working in a non-contact mode at room temperature. Phosphorus doped silicon cantilevers (model MPP-11123-10) with resonant frequency of about 275 kHz and approximate spring constant of 48 N/m were used. The back side of the cantilever was covered by 50 nm of aluminium. The nominal tip curvature of the used cantilever was less than 8 nm.

Capacitance voltage (CV) measurements are carried out by a set-up based on a Agilent 4284 LCR meter. CV measurements with slow DC voltage ramps of 25 mV/s are started in accumulation, the height of the AC signal is set to 25 mV (RMS). Silver contacts with diameters of 400-800 µm were evaporated on top of the sample using a shadow mask in order to realize metal-insulator-semiconductor (MIS) structures.

RESULTS AND DISCUSSION

A. XPS measurements

Chemical composition of obtained film was evaluated by XPS analysis. The XPS spectra of regions C1s, O1s and Si2p are given in Fig. 1. On the basis of the Gaussian functions spectra were deconvoluted into more peaks that correspond to different binding energies. The fitting results of the obtained spectra and their assignments are given in Table 1.

After the normalization of XPS spectra, the ratio of the elements contained in the investigated film was estimated. Spectra normalization were performed by dividing their areas by atomic sensitivity factors equal to 0.711, 0.296, and 0.283 for O1s, C1s, and Si2p, respectively. Basing on XPS analysis the ratio of particular elements within prepared film C:O:Si equals 2.7:1.9:1. According to those results, the ratio of silicon to oxygen atoms within examined material is very similar to SiO_2 and equals 1:1.9. Formation of the SiO_2 network is typical for the materials obtained by the sol-gel method. However, in the case of investigated sample the existence of the carbon atoms is of high importance. The contributions of the carbon in XPS spectra come not only from fullerene molecules incorporated into the material but mainly from aromatic rings in Ph-TriEOS and from methyl groups from Me-TriMOS and Ph-TriEOS that were not removed during the fabrication process.

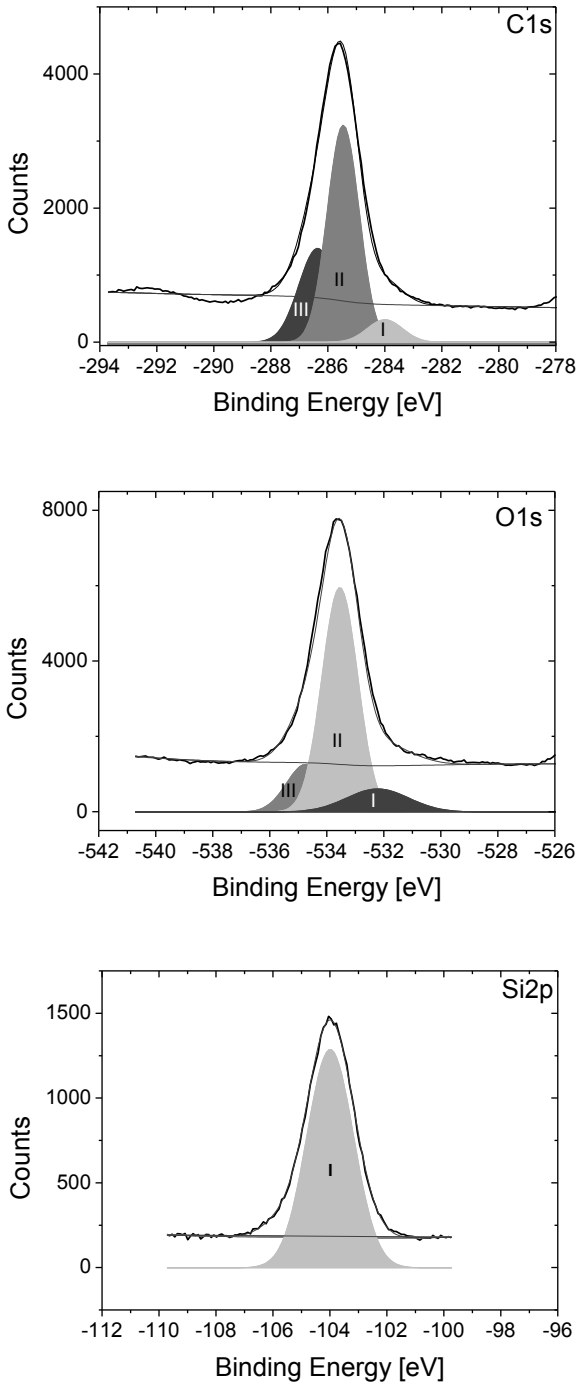

Fig. 1 XPS spectra of fullerene based material produced by sol-gel method. Regions: C1s, O1s, and Si2p are shown.

B. NEXAFS

NEXAFS data of the fullerene based sample are displayed in Fig. 2 (solid line) in comparison with a pure C_{60} film (dash line). Here, the TFY delivers bulk information while TEY is more surface sensitive.

In the case of C_{60} derived components, there is a particular mechanism causing a characteristic feature in the absorption data. Based on the electronic properties of the C_{60} molecules in all C_{60} derived compounds, there is a characteristic split in the lowest absorption band causing a three-peak structure [18, 19]. In our sample three peaks transitions located at 284.9 eV, 287.5 eV and 288.5 eV are found. In particular, the middle band appears at a higher photon energy than in pure C_{60} films.

TABLE 1
XPS INVESTIGATIONS OF THE SAMPLE OF FULLERENE BASED MATERIAL PRODUCED BY SOL-GEL METHOD. PEAK POSITION WERE IDENTIFIED ACCORDING TO THE LITERATURE CITED IN THE TABLE

Region	Peak number	Position [eV]	Percentage of the main peak area [%]	Assignment
C1s	I	-284	7.12	C-C Sp^2 [8]
	II	-285.46	61.41	C-C Sp^3 [9] C-C/C-H [10,11]
	III	-286.36	31.47	C-O [10, 12]
O1s	I	-532.23	12.68	O-H [13]
	II	-533.55	70.96	C-O[14] Si-O[15]
	III	-534.74	16.37	CO_2[16]
Si2p	I	-104	100	Si-O[17]

Considering small concentration of the fullerenes within the sol-gel material and significant shift of the middle band we presume that the main contribution to the features corresponding to the C1s-π* transitions comes from the phenyl groups of one of the precursors (Ph-TriMOS). According to the literature features in the range of 284 to 289 eV may be assigned to the C1s-π* transitions of the benzene derivatives [20]. Broadening of the feature near 287 eV may be caused by the contribution of the C1s-σ (C-H) resonances from the methyl group [21]. Nevertheless, we cannot exclude the contribution of the C1s-π* transitions of the fullerenes in the NEXAFS spectra as shown in Fig. 2.

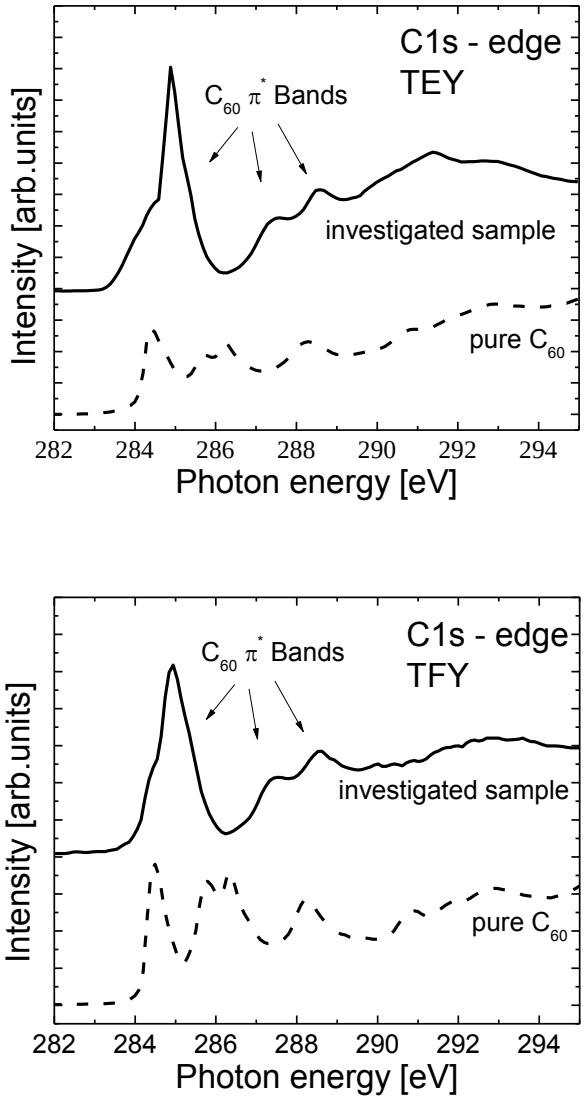

Fig. 2 Comparison of NEXAFS data of samples fabricated by evaporation (dashed line) and sol-gel method (solid line), respectively: the spectra show the typical C60 absorption features on the surface TEY and also in the bulk TFY.

C. FTIR

The chemical composition of organo-silica matrix of the sample was investigated with FTIR spectroscopy. Particular bands are recognized from the $Si-CH_3$ group: 780 cm^{-1}, 897cm^{-1}, 1273 cm^{-1} [3]. The bands at 431 cm^{-1} and corresponding at 2978 cm^{-1} are assigned to C-H bond [22]. The band appearing at 699 cm^{-1} is recognized as coming from Si-C bond. Characteristic bands are assigned to Si-O-Si structure: 487 cm^{-1}, 1039 cm^{-1}, 1134 cm^{-1}. The band at 1595 cm^{-1} is recognized as characteristic for double bond C=C from the phenyl ring. The flat, broad band around 3400 cm^{-1} is attributed to a group of signals coming from stretching vibration of phenyl ring's C-H bonds, to the Si-OH groups and H_2O molecules presence [23].

D. Thickness measurements

To perform thickness measurements of the film a part of the investigated material was removed by a scalpel in order to reveal SiO_2 substrate. AFM scan was started in the place where AFM tip scanned both the substrate and the material which thickness was to be measured.

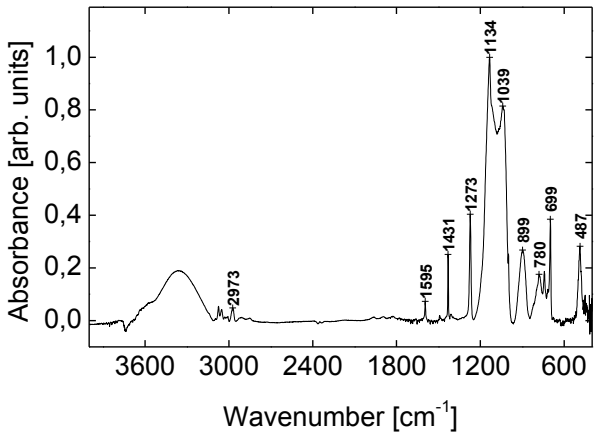

Fig. 3 FTIR spectra of organo-silica matrix.

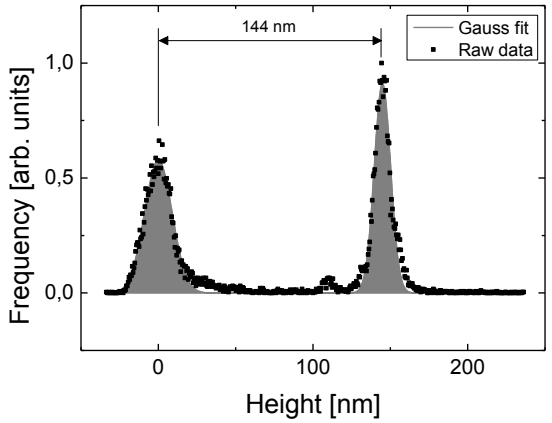

Fig .4 Surface height histogram of the region with both the substrate and the investigated material. Raw histogram data (black squares) were fitted by a Gauss functions (dark grey). The marked difference between peaks indicates the height of the deposited material.

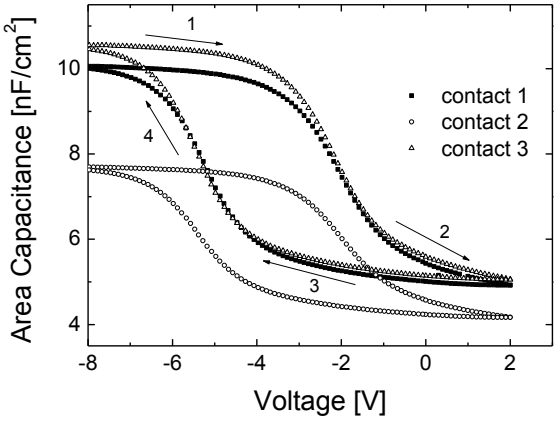

Fig. 5 CV measurement on a MIS stack consisting of C60 derived compound. The measurements were taken at a frequency of 100kHz at different contacts of the sample. The measurement direction is illustrated by the arrows.

The fast scanning direction was perpendicular to the line dividing the two materials giving rise to a clear step height difference in every measurement line. As a basis for the reliable height measurements the surface height histogram analysis was chosen (Fig. 4) [24]. Clear two peaks in the surface height histograms can be noticed. Both peaks were fitted with Gauss functions and the peaks centre position were acquired from the fits. The step height equals the difference between the peaks centre positions. For the measured sample height of the deposited material was estimated to 144 nm. Height investigations require precise AFM levelling as a small misalignment between measuring axis and sample axis increases error in height measurements [25].

E. CV measurements

CV measurements were performed on a MIS stack as described in experimental section. Fig. 5 depicts results recorded at a frequency of 100 kHz at three different contacts positions of this sample. The CV curves show two aspects about the need of a strong quality improvement of the layer. The fist aspect is that the dispersion of the area capacitance indicates either a thickness and/or a porosity distribution inhomogeneity. The open porosity of this layer is estimated using ellipsometric porosimetry to approximately 18%. The pore size distribution is classified as mesoporous (mean pore size in the range of 2 nm – 50 nm) [26]. Large hysteresis in the CV measurements indicates the presence of movable charges inside the layer. That phenomenon can be due to the Si-OH groups and H_2O molecules in film pores [27] (FTIR bands in the range of 3600-3200 cm^{-1}). This leads to a certain capacitance instability when the material is used in interconnects. In this stage of investigations we have not yet performed annealing steps which might lead to the avoidance of moveable charges inside the layers and, therefore, to an improved performance of the stack.

The *k*-values were determined from the accumulation capacitance of the CV measurements. At two of the contacts we calculate a relative dielectric constant in the range of 2.3 to 2.5, on the other one it is about 20% lower. Here the SiO_2 thickness of 100 nm and the thickness of 144 nm of the low-*k* layer as measured by AFM step measurements (see above) are taken into account. This results demonstrate that our fullerene based material may exhibit desired values for ULK application, however the layer quality should be improved by modified preparation methods.

CONCLUSIONS

We obtained fullerene based low-*k* material by means of the sol-gel method. Spectroscopic investigations confirmed, that the produced SiO_2 network is functionalized by the methyl and phenyl groups. For that reason the contributions to the carbon species existing within the film comes not only from the fullerenes but mainly from the phenyl rings and methyl groups. XPS analysis showed, that the overall amount of the carbon-like species within the sample is relatively high and the ratio of carbon, oxygen and silicon atoms within obtained film equals 2.7:1.9:1. We presume that the low dielectric constant is due to the high concentration of the organic groups (methyl and phenyl) and the material porosity. In order to reduce further the dielectric constant the concentration of the fullerene molecules should be significantly increased. Nevertheless the homogeneity of the layer needs further improvement. As an outlook we are going to produce fullerene-based material while omitting the sol-gel procedure. In order to obtain better distribution of the fullerene molecules within the sample and its higher concentration we are going to use nitrogen containing siloxane precursors.

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